ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 12, pp. 2472–2474. © Pleiades Publishing, Ltd., 2014.
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LETTERS TO THE EDITOR

Azinyl Derivatives of Ferrocene for Preparation of Poly(Methyl Methacrylate) with Enhanced Properties

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Received October 28, 2014

Abstract—Influence of 1-[pyridyl-2]-, 1-[quinolin-2-yl]-, 1-[acridin-9-yl]-, 1-[pyrazin-2-yl]-, and 1-[pyrimid-4-yl]-ferrocenes on heat and thermomechanical properties of the produced poly(methyl methacrylate) has been studied.

Keywords: azinyl ferrocene, poly(methyl methacrylate), radical polymerization, initiator, thermal properties, thermomechanical properties

DOI: 10.1134/S1070363214120251

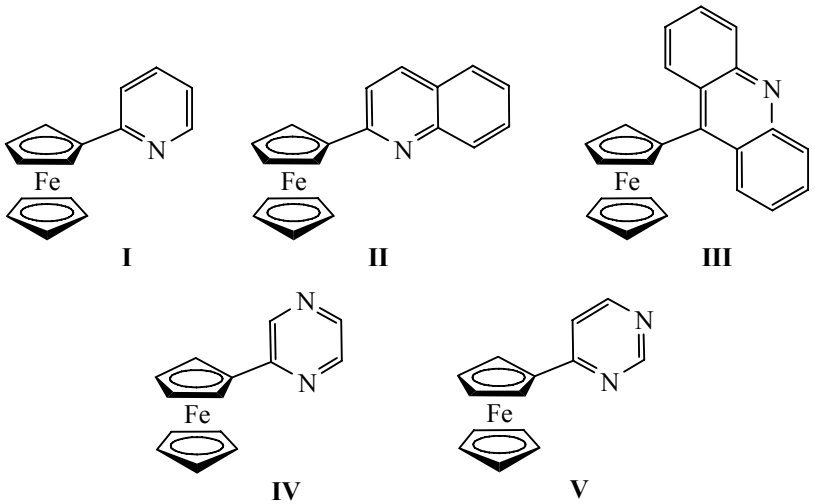
Metal complexes are highly promising for application in controlled polymerization processes and for preparation of polymeric materials with enhanced physico-chemical properties.

Earlier we reported on the effect of 1-[pyridyl-2]-, 1-[quinolin-2-yl]-, 1-[acridin-9-yl]-, 1-[pyrazin-2-yl]-, and 1-[pyrimidin-4-yl]ferrocenes **I**–**V** on kinetic features of radical polymerization of methyl methacrylate and molecular parameters of the prepared polymer [1, 2] (Scheme 1).

It was demonstrated that the metal complexes **I**–**V** combined with diacyl peroxides (benzoyl peroxide or lauryl peroxide) form highly efficient initiating systems, more active than the systems based on unsubstituted ferrocene [3–5], allowing for fast polymerization with high yield at lower temperatures (30–60)°C. The spectral studies confirmed that both ferrocenyl and heterocyclic fragments of compounds **I**–**V** affected the coordination with peroxide initiator [2].

The mentioned ferrocenes did not interact with azobisisobutyronitrile AIBN but the overall polymerization rate of methyl methacrylate polymerization was somewhat increased, pointing at the influence of the azinyl ferrocenes on the chain growth processes in addition to that on the initiation step [2].

Scheme 1.



Depending on the conditions, application of ferrocenes **I**–**V** allowed preparation of poly(methyl methacrylate) with weight-average molecular mass of 4×10^5 to 2.5×10^6. The polydispersity index M_w/M_n was of 1.3–3.0 depending on the monomer conversion, being in general lower than in the case when the radiacl initiator was used alone (M_w/M_n = 2.0–4.0). Molecular mass parameters confirmed the influence of the additive on the chain growth and chain termination steps [1, 2].

Hence, the azinyl ferrocenes **I**–**V** are promising components of initiating or catalyzing systems for application in radical polymerization of vinyl monomers; the additives affect all the polymerization stages, including initiating, chain growth and chain termination. The more detailed study of the polymers prepared using such additives has been required. In view of that, this work aimed to investigate the ferrocenes **I**–**V** effect on thermal and thermomechanical properties of poly(methyl methacrylate).

It was stated that the onset of heat-induced decomposition (corresponding to 1% mass loss) of poly (methyl methacrylate) prepared in the presence of radical initiator (benzoyl peroxide or AIBN) and complexes **I**–**V** was up by 40–65°C (from 220–225 to 265–285°C) as compared to that of the reference sample prepared in the presence of the radical initiator alone. With conversion increasing from 10 to 80%, the heat resistance of the polymer product was also growing by 10–20°C at the average. The low-temperature peak in the differential thermograms disappeared, similarly to the case of using unsubstituted ferrocene [3, 5].

The two possible reason of enhanced heat resistance of the polymers prepared in the presence of ferrocenes **I**–**V** were as follows. First, that could be due to the changes in stereochemical composition of the macromolecule (increase of the syndiotactic structures). However, the variation of the content of syndiotactic fragments upon introduction of azinyl ferrocenes in the polymerizing mixture was minor (62–64% as compared to 55–56% in the case of the reference polymer [2]); that was typical of other metallocenes as well. Another reason could be that using metal complexes as component of the initiating/catalyzing system could enhance stability of the end fragments of the polymer chain. That was confirmed by mass spectrometry data. In particular, decomposition of poly(methyl methacrylate) prepared in the presence of equimolar amounts of the complexes **I**–**V** and AIBN or benzoyl peroxide yielded the products with relatively high molecular mass, absent in the case of the reference polymer. Note that prior to the experiment the polymer was thoroughly purified of the traces of the additive and the catalyst by repeated re-precipitation, thus avoiding direct influence of any impurity on the observed properties.

Study of thermomechanical properties of the prepared poly(methyl methacrylate) (conversion of about 95%) showed that introduction of the complexes **I**–**V** into the polymerizing mixture practically did not influence the polymer glass transition temperature (T_g), being of 105–110°C in the case of all the studied samples including the reference ones. However, the flow temperature (T_f) was up from 185–190 to 255–260°C. That enhanced the (T_f–T_g) range from 80–85°C (reference) to 150–155°C (the polymer prepared in the presence of compounds **I**–**V**).

To conclude, using azinyl ferrocenes allowed preparation of poly(methyl methacrylate) with enhanced thermal and thermomechanical properties.

EXPERIMENTAL

Methyl methacrylate (Fluka) was twice distilled under reduced pressure; the fraction with bp 42°C (120 mmHg), n_D^{20} 1.4130, and d_4^{20} 0.936 g/mL was used for polymerization.

Benzoyl peroxide and AIBN were recrystallized from ethanol three times and dried in vacuum at room temperature to constant mass. Azinyl derivatives of ferrocene **I**–**V** were prepared and purified as described elsewhere [7]. Purity of the compounds was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Poly(methyl methacrylate) was prepared by bulk radical polymerization. To do so, a mixture of methyl methacrylate, initiator, and the metal complex was put in an ampoule, degassed via thrice freeze-thawing to a residual pressure of 1.3 Pa, sealed, and incubated at 60±0.1°C till required conversion of polymer was reached. The formed product was dissolved in acetone and precipitated with 10–15-fold excess of methanol. The re-precipitation was repeated three times to wash out the residual initiator and metal complex. Equimolar amount of the metal complex and the initiator were applied (0.001 mol/L each).

The polymer microstructure was analyzed by means of ^{1}H NMR spectroscopy [8]. Content of the

triads was calculated from integral intensity of the corresponding α-methyl signal (1.17 ppm, *iso*-; 0.98 ppm, *hetero*-, and 0.79 ppm, *syndio*-).

Dynamic thermogravimetry analysis of the 100 mg specimens was performed using a Q-1000 MOM derivatograph (Hungary) at heating rate of 5 deg/min, in air or in nitrogen atmosphere.

Mass spectra were registered using a Thermo Finnigan MAT 95 XP instrument.

Thermomechanical analysis was performed using an automated station based on a H307 bi-coordinate potentiometer taking advantage of penetration technique at constant load of the 80 mg sample (20 g/mm^2) and at heating rate of 2.7 deg/min, in air.

ACKNOWLEDGMENTS

Authors are grateful to O.N. Chupakhin and I.A. Utepova (Postovskii Institute of organic synthesis, Ural Branch, Russian Academy of Sciences) for the provided samples of the ferrocenes.

This work was financially supported by Russian Foundation for Basic research (project no. 14-03-00260-a).

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